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(21) International Application Number: PCT/CA91/00160 (22) International Filing Date: 13 May 1991 (13.05.91) (60) Parent Application or Grant (63) Related by Continuation US 208,716 (CIP) Filed on 7 June 1988 (07.06.88) (71) Applicant (for all designated States except US): BUDRA RE- SEARCH LTD. [CA/CA]; P.O. Box 6958, Stn. "D", Calgary, Alberta T2P 2G2 (CA). (72) Inventors; and (75) Inventors/Applicants (for US only) : MAHADEV, Kalabeer- appa, N. [CA/CA]; 131 Edforth Crescent N.W., Calgary, Alberta T3A 3X5 (CA). IRANI, Jamsheed, Phiroze [CA/ CA]; 155 Lake Adams Crescent S.E., Calgary, Alberta T2P 2G2 (CA). GUNNING, Harry, E. [CA/CA]; 14815 - 64th Avenue, Edmonton, Alberta T2V 2H8 (CA).		(74) Agent: FRENCH, David, J.; P.O. Box 2486, Stn. "D", Ot- tawa, Ontario K1P 5W6 (CA). (81) Designated States: AT, AT (European patent), AU, BB, BE (European patent), BF (OAPI patent), BG, BJ (OAPI patent), BR, CA, CF (OAPI patent), CG (OAPI patent), CH, CH (European patent), CI (OAPI patent), CM (OAPI patent), DE, DE (European patent), DK, DK (European patent), ES, ES (European patent), FI, FR (European patent), GA (OAPI patent), GB, GB (Euro- pean patent), GR (European patent), HU, IT (European patent), JP, KP, KR, LK, LU, LU (European patent), MC, MG, ML (OAPI patent), MR (OAPI patent), MW, NL, NL (European patent), NO, PL, RO, SD, SE, SE (European patent), SN (OAPI patent), SU, TD (OAPI patent), TG (OAPI patent), U- Published <i>With international search report.</i>
(54) Title: CATALYST AND PROCESS FOR REMOVAL OF SULPHUR COMPOUNDS AND NITROGEN OXIDES FROM FLUID STREAMS (57) Abstract The invention comprises a regeneratable catalyst that is capable of providing a reactive oxygen to partially oxidize sulphur- containing compounds to produce sulphur. It includes a method for removing sulphur compounds including both sulphur oxides and hydrogen sulphide from a fluid stream and decomposing such compounds to produce sulphur. Sour natural gas can be sweetened effectively by this invention, and sulphur can be prepared thereby. The catalyst is preferably formed by impregnating alkali metal sulfide and sulfide(s) or selenide(s) of metal(s) showing polyvalent and/or amphoteric character, e.g. Zn, etc. on a microporous type support (e.g., alumina). Its activity is sustained by exposure to a source of oxygen, such as air, oxygen sulphur dioxide or nitrogen peroxide and the like. A method is also described by which sulphur dioxide may be absorbed from flue gas and converted to sulphur, while higher oxides of nitrogen and carbon dioxide are being absorbed for subsequent recovery, utiliz- ing a catalyst that has been conditioned by prior exposure to a reducing gas.		

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CATALYST AND PROCESS FOR REMOVAL OF SULPHUR
COMPOUNDS AND NITROGEN OXIDES FROM FLUID STREAMS

Field of Invention

The desirability of identifying an effective means
5 for removing sulphur compounds from fluid streams will be
readily appreciated. This invention comprises a novel
method and catalyst for effecting such removal and the
subsequent treatment of such sulphur compounds to produce
10 elemental sulphur. More particularly this invention is
applicable to the removal of hydrogen sulphide and other
sulphur compounds from sour natural gas, and other fluid
streams, and the conversion of the sulphur therein to
elemental sulphur.

By the same process applied in a different order,
15 the invention may be used to remove certain oxygen
compounds from gas streams, and particularly to remove
sulphur dioxide, sulphur trioxide, nitrogen trioxide,
nitrogen peroxide, nitrogen pentoxide and carbon dioxide
from flue gases.

20 Background of the Invention

Sulphur compounds are often considered to be
undesirable compounds in gas mixtures and other fluid
streams. The most common example of this is that of
natural gas containing hydrogen sulphide. Natural gas may
25 also contain as undesirable sulphur compounds, quantities
of carbonyl sulphide, carbon disulphide, mono and dialkyl
sulphides, alkyl-type disulphides and thiophenes.

The removal of such sulphur-containing compounds
from gas streams has been addressed by a number of methods
30 in the past. These methods generally rely on direct
reactions with the sulphur compounds, or proceed to first
separate the sulphur compounds from the gas stream by an
absorption stage. In the latter case, the sulphur and
other constituent elements of the absorbed compounds must
35 then be extracted, if the absorptive medium is to be
regenerated. A particularly desirable regenerative
process would be one which produces elemental sulphur from
the same reaction bed.

Various systems have been explored with the view of
40 removing hydrogen sulphide from gas streams and producing

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elemental sulphur. The Claus process, as currently applied, is a complex multi-stage system involving the absorption of the hydrogen sulphide in an amine absorbent, flashing off H_2S from the amine, followed by the burning of part of the hydrogen sulphide to sulfur dioxide, and subsequently reacting the hydrogen sulphide with the sulfur dioxide to produce sulphur as the final product as elemental sulphur.

It would be obviously desirable to provide a method for removal of hydrogen sulphide and other sulphur-containing compounds from a fluid stream at ambient temperatures followed by the subsequent conversion at moderate temperatures of the sulphur compounds into elemental sulphur and other non-sulphur containing decomposition products.

Flue gases generally include appreciable quantities of oxides of sulphur, nitrogen peroxide and carbon dioxide. It would be desirable to have a process which effectively removes such compounds from flue gas, and allows for their separation and subsequent utilization.

Objects of the Invention

It is therefore an object of the invention to remove sulphur compounds from a fluid stream and recover elemental sulphur therefrom. It is further an object to do so in the same reaction bed.

It is also an object of the invention to provide a means which will allow removal and decomposition of hydrogen sulphide from a gas stream, at temperatures below the condensation point for sulphur and the separation of the sulphur so produced, at a modestly elevated temperature (circa $250^{\circ}C$ - $600^{\circ}C$).

A further object of the invention is to remove sulphur dioxide, nitrogen trioxide, nitrogen peroxide, nitrogen pentoxide and carbon dioxide, separately or collectively from a gas stream, and then to convert the sulphur dioxide to sulphur, convert the nitrogen peroxide and other oxides to nitric oxide, and separately release the carbon dioxide, nitric oxide and sulphur so produced for subsequent utilization.

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These and other objects of the invention will become apparent from the description of the invention and claims thereto which follow.

Summary of the Invention

5 In its most general aspect this invention comprises a regeneratable catalytic composition comprising a support having associated therewith a non-gaseous, non-fluid substance capable of retaining and providing reactive oxygen for reaction with oxidizable substances
10 brought into contact with such composition, and thereafter capable of being replenished with reactive oxygen by exposure to a source of oxygen. As such the invention may be characterized as a "regeneratable solid peroxide" - type of composition, and includes methods by which such
15 composition may be employed

 More particularly, this invention comprises a specially prepared bed for absorbing sulphur compounds, and particularly hydrogen sulphide or oxides of sulphur from a fluid stream and subsequently decomposing such
20 compounds into elemental sulphur. This same bed may be used to absorb oxides of nitrogen, and particularly nitrogen peroxide but excluding nitrous oxide, and absorb as well carbon dioxide from a gas stream for subsequent separate recovery.

25 A suitable bed for treating non-oxide compounds of sulphur comprises a support adapted to accommodate or absorb such non-oxide sulphur compounds therein, and particularly hydrogen sulphide, which support contains an alkali metal sulphide or selenide together with a sulphide
30 or sulphides, (or selenide/s) of metals showing polyvalent and/or amphoteric character deposited therein, and has been rendered thereby capable of providing internally available "reactive oxygen", e.g. having peroxide-like characteristics, after exposure to a source of oxygen.

35 The use of "and/or" in the above discussion, and throughout this disclosure, is to be taken in its non-exclusory sense. Thus, a mixture of both amphoteric and polyvalent compounds may be used in place of either alone, and a metal which is both amphoteric and polyvalent is
40 intended to be included by this expression.

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The reference to "reactive oxygen" is intended to refer to oxygen in an elevated energy state whereby the oxygen is available to react with the non-sulphur component of the compounds being treated in some cases
05 even at ambient temperatures so as to release sulphur.

Amphoteric metals are those metals which show a capacity to react both with acids and bases.

Examples of amphoteric or polyvalent metal sulphides or selenides suitable for use in this invention
10 include, amongst others, sulphides or selenides of metals from the group consisting of zinc, manganese, iron, copper, cobalt, aluminum, vanadium, molybdenum, tin and nickel as well as mixtures thereof. Examples of alkali metals suitable for use in this invention include lithium,
15 potassium, sodium, rubidium and cesium, as well as mixtures thereof.

A bed so constituted and suitably conditioned according to this invention is also adapted to remove and decompose sulphur compounds such as carbonyl sulphide,
20 carbon disulphide, mono and dialkyl sulphides, alkyl-type disulphides, and thiophenes from a gas or liquid stream by contacting such a stream with the aforesaid bed, at ambient temperatures. This same bed is capable of absorbing oxygen-containing compounds to provide reactive
25 oxygen. Suitable compounds for this effect are sulphur dioxide, sulphur trioxide and nitrogen oxides, including nitrogen trioxide, nitrogen peroxide and nitrogen pentoxide but excluding nitrous oxide, i.e. the "higher" oxides of nitrogen.

30 One method of preparing the bed is by:

- (a) preparing in aqueous solution a mixture of an alkali metal salt and a polyvalent and/or amphoteric metal salt;
- (b) impregnating a support with the mixture described
35 in (a) above;
- (c) drying the support after it has been so impregnated;
- (d) sulphiding (or seleniding) the impregnated support at ambient or higher temperatures by exposing it
40 to a gas stream containing a reactive sulphur (or selenide) compound such as hydrogen sulphide,

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carbonyl sulphide or carbon disulphide, or their selenide equivalents, which has the effect of converting the metal and alkali salts to sulphides or selenides;

- 5 (e) heating the impregnated support at an elevated temperature to drive off excess sulphur, or selenium so as to thereby form the bed in its pre-oxygenated form; and then,
- 10 (f) exposing the bed to a source of oxygen such as, by way of example, to atmospheric oxygen or an oxygen-containing compound such as sulphur dioxide or nitrogen peroxide, whereby reactive oxygen becomes available within the bed and thereby create the bed in its oxygen-activated form.
- 15 This invention further comprises the production of elemental sulphur by the method of exposing, at a temperature below the vaporization point of sulphur, a gas stream containing non-oxide compounds of sulphur, and particularly for example hydrogen sulphide, to the
- 20 oxygenated bed and then regenerating the bed. The bed is regenerated by first applying heat at a predetermined elevated temperature or temperatures (such as in the range of 250°C to 600°C) bed in the presence of a substantially non-reactive sweep gas. This will drive off any residues
- 25 of the oxidized non-sulphur component of the sulphur compound, this being in the case of hydrogen sulphide water, and elemental sulphur thus purging the bed of these substances. The regeneration process is then completed and the bed reconditioned by exposure of such bed to an
- 30 unreactive sweep gas containing a source of oxygen. Optionally, a source of oxygen may also be provided during the initial purging step either as an alternative to subsequent treatment with oxygen, or in addition.

- The amount of oxygen provided with the sweep gas
- 35 in the final step may range from a stoichiometric amount necessary to oxidize the sulphur compound to be subsequently treated and release elemental sulphur, up to a concentration of about 25%, although this is not necessarily limiting in all cases. In certain cases
- 40 excess oxygen and highly oxidizing agents such as hydrogen

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peroxide must be avoided to prevent damage to the bed.

This invention further comprises the method by which the oxides of sulphur, particularly sulphur dioxide and the oxides of nitrogen, particularly nitrogen peroxide but excluding nitrous oxide, are removed from a gas stream. This is arranged by permitting these compositions to be absorbed within and impregnate a bed comprised of a microporous support which contains an alkali metal sulphide or selenide, and a sulphide or selenide of metals showing polyvalent and/or amphoteric character, which bed has been depleted of reactive oxygen by exposure to a reducing gas, preferably hydrogen sulphide. The bed, so impregnated, is then exposed to a reducing gas, such as to a stream of hydrogen sulphide, whereby the absorbed sulphur dioxide and hydrogen sulphide are converted to water and elemental sulphur, and the nitrogen peroxide and other nitrogen oxides are converted to nitric oxide. These products are then purged from the bed by heating the bed in the presence of a sweep gas, thus returning the bed to a condition whereby it is ready to repeat the cycle.

By a further feature of the invention, the bed containing the above referenced activating ingredients, when depleted of internally available reactive oxygen, is capable of absorbing at ambient temperatures quantities of carbon dioxide. The absorption of carbon dioxide can be carried-out either separately or in conjunction with the absorption of the other referenced oxides. Once carbon dioxide has been absorbed, it can be released and recovered by heating the bed.

These and further features of the invention and its various aspects will be apparent from the description of the examples and test results set forth in the following.

Summary of the Figures

Figure 1 is a graph showing the effect of temperature on the rate of desorption of hydrogen sulphide from a series of sample catalytic beds which have been saturated with hydrogen sulphide.

Figure 2 shows the capacity of a bed according to the invention to become loaded with hydrogen sulphide and

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sulphur dioxide as a function of pressure.

Characterization of the Catalyst within the Bed

The active catalyst within the bed that provides reactive oxygen is believed to be characterized by a chemical having as its constituents a complex containing the combination of an amphoteric and/or polyvalent metal (hereinafter referred to as the "metal"), an alkali metal, (hereinafter referred to as the "alkali"), sulphur or selenium and the capacity to retain an active oxygen-containing moiety that contains an available reactive oxygen group. This complex should preferably be formed within a microporous support having a relatively high surface area and a microporosity adapted to receive the sulphur or oxide compound to be decomposed.

Alumina is considered a preferred support because of its high surface area. Also, it is believed, without limiting the invention as demonstrated, that alkali metal incorporated into the support to form the active complex will react with alumina to form an alkali aluminate and facilitate bonding of the active complex to the carrier. Alumina may thereby provide an etchable substrate upon which active sites may be more readily formed.

The process of solvent extraction using methylene chloride, when applied to an activated catalyst containing manganese and potassium sulphides on alumina (Alcoa #S-100), showed the following extracted constituents:

free manganous sulphide	- 51% (by weight)
free potassium sulphide	- 18%
other constituents including potassium aluminate and potassium hydroxide	- 31%

An attempt to utilize methanol on the same catalyst produced inconclusive results as the constituents were apparently modified by the methanol as a solvent (perhaps by hydrolysis of the manganous sulphide) as was indicated by a change in colour of the solution from green to brown shortly after extraction.

It has been found that the catalyst is capable of decomposing a small portion of absorbed hydrogen sulphide without the addition of oxygen during the decomposition

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heating phase. The activity of the catalyst under such conditions, however, declines rapidly. It is believed that the catalyst is intrinsically capable of supplying small amounts of oxygen, but that this capacity is rapidly
5 depleted. This belief is supported by the observation that exposure of the catalyst to a reducing atmosphere causes catalytic decomposition activity to drop to virtually zero.

The provision of oxygen to the catalytic bed,
10 either while decomposition is occurring or upon regeneration of the catalytic bed has been found necessary to preserve or restore the activity of the catalyst. Thus while oxygen may be consumed in the decomposition cycle, it is readily restorable by exposure of the catalyst
15 thereafter to a source of oxygen in either molecular or compound form.

The ability of a microporous support, impregnated with the components which form the active catalyst, to absorb certain oxygen compounds has a separate utility. A
20 bed, prepared in accordance with the invention, will absorb not only molecular oxygen, but also sulphur dioxide, sulphur trioxide and nitrogen oxides, excluding nitric oxide. All of these compounds are capable of producing the reactive oxygen which is characteristic of
25 the invention.

This ability of the catalyst to become oxygen-activated with such compounds allows a catalytic bed, prepared in accordance with the invention, to be used to absorb such compounds from flue gas. The bed, once
30 saturated, may then be purged of such compounds by exposure to hydrogen sulphide, followed by heating in the presence of a sweep gas. In the case of sulphur dioxide, this compound is decomposed into water and elemental sulphur. Thus a major pollutant in flue gas can be
35 effectively removed from flue gas and converted to a valuable commodity.

Preparation of the Catalytic Bed - Method 1

Catalytic beds were prepared by two alternate
40 methods. The first method commenced by dissolving a

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predetermined amount of the alkali sulphide (sodium or potassium) in water sufficient to form the ultimate desired loading on the support and optionally boiling the solution. To this solution a molar equivalent amount of an amphoteric and/or polyvalent metal sulphide was added and the solution was boiled again until the volume was reduced to a point short of saturation. Then the support (generally in the form of Alcoa alumina spheres, #S-100) which had been dried by being heated to 250°C for 4 hours was added to the hot solution and mixed until all the solution was absorbed into the support. The partially prepared catalytic bed was then dried (using a nitrogen gas flow at 400°C) and cooled. The catalytic bed was then sulphided by exposure to a stream of 10% hydrogen sulphide in nitrogen or methane at ambient conditions until hydrogen sulphide was detected in the effluent and for at least one hour thereafter. It was then purged of excess sulphur by heating in a nitrogen gas flow at 400-500°C for a period of 0.5 to 1.0 hours to drive off free sulphur.

The partially prepared catalytic bed can also be sulphided by exposure first to a stream of 10% hydrogen sulphide in nitrogen or methane at 400°-500°C for 4 hours and then to a stream of nitrogen or methane at 400°-500°C to remove any excess sulphur. Some tests were run in which the conditioning gas was a 50/50 mixture of hydrogen sulphide and hydrogen and the active metal in the catalyst was manganese. This change in the nature of the conditioning gas considerably reduced its activity for the sample catalyst so prepared.

Preparation of the Catalyst - Method 2

A second method of preparing the catalytic bed was as follows. A sulphate, chloride or nitrate of a polyvalent and/or amphoteric metal was dissolved in an aqueous solution. The mixture was then heated to ensure rapid dissolution. (This, as above, is considered an optional step.)

The solution was then impregnated on a previously dried alumina support (Alcoa S-100, 1/4 in. spheres) and the impregnated support dried.

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A molar equivalent or greater amount of an alkali metal sulphide was then prepared in an aqueous solution and impregnated on the support. Again, heating was optionally employed to effect rapid dissolution.

5 The impregnated support was then heated to a temperature of 125°C for a period of 2 hours in order to fix the active ingredients within the support. This was followed by a washing of the impregnated support with water until all available alkali sulphate, chloride or
10 nitrate had been flushed from the support. The impregnated support was then dried at 125°C.

It is believed that at this stage most of the sulphate, chloride or nitrate originally impregnated has become converted to a sulphide of the amphoteric and/or
15 polyvalent metal. The available sulphate, chloride or nitrate salts of the alkali metal were washed out of the support because they were not believed to contribute to the activity of the catalyst and were thought to reduce the availability of active sites within the support. The
20 catalyst could be prepared without this step and still be capable of producing some decomposition of hydrogen sulphide. However, it is believed that the catalyst would generally show reduced activity without this step.

A stoichiometric amount of the alkali metal
25 sulphide was then prepared in an aqueous solution and impregnated on the carrier a second time. The impregnated support was finally dried at 125°C, and sulphided and purged of excess sulphur as described in Method 1.

Preparation of the Catalytic Bed - Further Alternate Methods

30 The above process has been carried-out with a variety of amphoteric and/or polyvalent metals in the form of sulphates, chlorides or nitrates and, it is believed, may be carried-out with any soluble salts of such metals including zinc, iron, vanadium, copper, nickel,
35 molybdenum, aluminum and manganese. It is believed that an active catalyst would be produced when these methods are carried out with all amphoteric and/or polyvalent metals. It is further believed that these methods would be effective in producing an active catalyst whether
40 sulphide or selenide salts of all amphoteric and/or

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polyvalent metals are used. Where less soluble compounds are employed, it may be appropriate to employ a basic aqueous solution in order to facilitate dissolution. A sufficiently basic solution can be created by adding
5 alkali hydroxide to the solution of the amphoteric and/or polyvalent metal salt and boiling this mixture.

Method 2 described above has been followed using either sodium or potassium as the alkali element. It is believed that lithium, rubidium or cesium sulphides may
10 also be substituted for the elements sodium or potassium, and still form an active catalyst using either methods.

It is further believed that selenium may be substituted for the sulphur in the alkali sulphide and still produce an active catalyst.

15 Based on sample tests, a satisfactory standard of performance for the catalyst in terms of both absorptive and decomposing capacity can be obtained with an approximate 1:1 molar ratio between the metal and alkali components, and a similar 1:1 molar ratio where an alkali
20 hydroxide is additionally employed.

Absorptive capacity for hydrogen sulphide is maximized for various metal sulphides at different levels of impregnation of the support. For example, this occurs between the 0.5% to 2.5% loading (by weight) range for a
25 catalyst incorporating a zinc sulphide/sodium sulphide mixture deposited by Method 1 on the Alcoa carrier (S-100 spheres).

Preparation of the Catalytic Bed - Activation with Oxygen

The bed may be activated in conjunction with the
30 sulphiding steps by exposing it, as an optional first step, at ambient or higher temperatures to an unreactive gas containing hydrogen sulphide, followed by heat treatment in an unreactive sweep gas at a temperature of 250°C-700°C containing an amount of oxygen as referenced
35 above. Alternately, after treatment with the sweep gas at elevated temperatures the bed may be exposed to oxygen at temperatures down to ambient conditions.

"Unreactive" is used here and throughout in the sense of a gas that does not substantially react in this
40 system.

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It is most desirable that the activating gas streams not contain appreciable amounts of compounds or elements, such as hydrogen, which will have a major reductive effect on the activity of the catalyst. It is also important for the treatment of non-oxide compounds of sulphur that the catalyst be exposed by the conclusion of the conditioning process to sufficient oxygen to ensure that reactive oxygen will be available within the catalyst to render it activated.

The source of oxygen may be either atmospheric or molecular oxygen, or may be a compound such as sulphur dioxide or nitrogen peroxide. All three of these sources have been found to produce, within the catalytic bed, the reactive oxygen which is a characteristic of the invention.

Sweetening, Decomposition, Purging and
Reactivation Procedures

The procedure followed to verify and quantify the production of sulphur from hydrogen sulphide was as follows.

A sample of a catalytic bed that had been purged of free sulphur and hydrogen sulphide by regenerating it at 400°C under an unreactive sweep gas (nitrogen or methane) and then activated by exposure to oxygen was weighed while placed in a reaction tube. A measured volume of unreactive gas containing a known percentage of hydrogen sulphide was then passed over the catalyst bed at a specific temperature, usually ambient, to remove the hydrogen sulphide from the gas stream. This was designated as the "sweetening" cycle. The length of exposure was either that required to produce an indication of hydrogen sulphide "breakthrough" at the exit end (as measured by the blackening of standardized lead acetate paper, or other standard methods), or some lesser period of time. A run to breakthrough was said to have saturated the bed. A run carried to a point short of saturation was designated as a "partial run".

The catalytic bed in its tube was then weighed to determine either the saturation loading of the bed, or the partial loading of the bed, in terms of its absorption of hydrogen sulphide.

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Throughout all experiments, the catalytic beds utilizing molecular sieves or alumina supports showed a capacity in the foregoing sweetening phase of maintaining the hydrogen sulphide level in the out-flowing stream
5 below the measurable threshold vis, 1 part per million prior to breakthrough.

The catalytic bed in its reaction tube was then put through the purging phase by exposing the bed to an unreactive sweep gas (nitrogen or methane) at a specific
10 temperature above the vapourization point for elemental sulphur for a period of time. The bed may then be reactivated by exposing it to a source of oxygen. This may be done, for example, by utilizing a sweep gas containing oxygen at levels of 0.01 to 25%. Oxygen may
15 also be supplied in the form of sulphur dioxide or nitrogen peroxide. Alternately, reactivation by exposure to a source of oxygen may be effected separately, after the purging phase is complete.

It has been found that with certain metals, such
20 as manganese, that the catalytic bed deteriorates if exposed to excessive levels of oxygen, e.g. over 10%. This may, it is believed, be due to the formation of a sulphate. The catalyst in such a case was restored to activity on re-exposure to hydrogen sulphide. However, it
25 is believed that the concentration of oxygen should preferably be limited in order to avoid such deleterious effects.

The sweep gas exiting the catalytic bed was caused to pass through a portion of the reaction tube that was
30 maintained at room temperature. During this process, when carried out with the bed at temperatures over about 250°C - 300°C, sulphur consistently condensed on the inside walls of a cooler, exit portion of the reaction tube in a condensation zone. Sample tests with glasswool placed
35 downstream of such deposits indicated that further sulphur could not be collected by condensation from the cooled exiting gas stream beyond the condensation zone.

A further procedure followed in some experiments was to collect the exiting sweep gas during the
40 regeneration step and then determine its hydrogen sulphide

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concentrations by gas chromatography. As further discussed below, little or no hydrogen sulphide was detected in the regeneration phase when the catalyst bed was only partially loaded with hydrogen sulphide, well
5 below the saturation level for the bed. For higher loadings and approaching saturation, much more hydrogen sulphide was detected in the regeneration stage of treatment.

After sulphur ceased to be forming further within
10 the cooler portion of the reaction tube, the tube and bed were reweighed. Comparisons of this weight with the weight of the tube following sweetening showed that virtually all of the sulphur remained in the system, up to this point. Then heat was applied to the outside portion
15 of the reaction tube where sulphur had deposited and the sweep gas flow was maintained. This procedure was continued until all of the sulphur in the reaction tube had been vapourized and carried out of the tube. The reaction tube and bed were then reweighed.

20 The catalyst bed, for purposes of experimental certainty, was then put through a super-purging phase by performing the previous procedure at 400-500°C for 1-2 hours. This step was shown through tests at higher temperatures to be capable of completely purging the
25 catalyst bed of remaining traces of free sulphur and residual hydrogen sulphide.

The inclusion of amounts of oxygen in the sweep gas during the super-purging phase was not found to be essential if it had been previously present as part of the
30 earlier treatment. Apparently, if sufficient oxygen is available during the normal purging phase, then the catalyst is reactivated. However, no deleterious effects occurred where oxygen was present on the super-purging phase as well. If insufficient oxygen was present during
35 the purging or super-purging phases, then oxygen should be supplied to the bed as a further step, which may be carried out at room temperature.

Oxygen may be supplied to the bed either in its molecular form, or in a compound such as sulphur dioxide
40 or nitrogen peroxide. Sulphur dioxide has been found to

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produce a much higher deposition of reactive oxygen within the catalyst. The use of sulphur dioxide also increases the absorptive capacity of the bed with respect to hydrogen sulphide.

5 The exposure of alumina to sulphur dioxide would normally be expected to result in the production of aluminum sulphite. If oxygen is present, as well, then aluminum sulphate will likely form. Where, however, alumina has been treated by the deposition therein of the
10 combination of sulphide or selenide salts of amphoteric or polyvalent metals combined with sulphite or selenide salts of alkali metals, the tendency of the alumina to form aluminum sulphite or sulphate is believed to be significantly reduced.

15 From the foregoing procedures calculations were made to determine the extent to which the hydrogen sulphide was converted to sulphur. The quantity of hydrogen sulphide absorbed in the catalyst bed was calculated based both on the gas flow rate, and on the
20 gain in weight of the bed and tube during the sweetening phase. The quantity of sulphur produced was obtained from the heat-vaporization procedure. The actual quantity of hydrogen sulphide decomposed was also determined by the difference between the volume of hydrogen sulphide
25 absorbed by the catalyst, and the volume of hydrogen sulphide collected by a gas bag during the regeneration. Of these methods, the mass of sulphur vaporized off the interior of the reaction tube was taken as the more reliable measure of the minimum decomposition that had
30 occurred.

Absorption of Sulphur Dioxide and Other Oxygen Compounds

 The procedure of utilizing the bed first to absorb hydrogen sulphide followed by reactivation with sulphur dioxide may be reversed or shifted in order. Thus, where
35 it is desired to remove sulphur dioxide from a gas stream the bed is first purged of sulphur dioxide by exposure to hydrogen sulphide, then purged of sulphur by heating in the presence of an oxygen-free sweep gas. So prepared, the bed will then readily absorb sulphur dioxide to the
40 limit of saturation. Once the bed has been saturated with

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sulphur dioxide, it may be again exposed to hydrogen sulphide to purge it of the sulphur and water that is thereby formed.

5 The bed will similarly absorb sulphur trioxide, which can be converted to produce sulphur by the same steps.

10 It has been found that when sulphur dioxide is used as the source for oxygen, it is relatively tenaciously contained within alumina-type supports. This enables an activated bed to be prepared in one location, and then transported to another. Similarly where the bed is only partially saturated with hydrogen sulphide in the sweetening cycle, the bed material is readily transportable.

15 The bed, suitably depleted of oxygen has an affinity to absorb not only the oxides of sulphur, but also nitrogen peroxide and similar higher oxides (but not nitrous oxide), and carbon dioxide. Further, the bed has the capability of absorbing all of these classes of oxides
20 simultaneously.

Absorption of Nitrogen Peroxide

The source of oxygen may also be nitrogen peroxide. This is a component often found in the products of combustion and in flue gases.

25 When nitrogen peroxide is used as the source of oxygen, subsequent exposure of the bed to hydrogen sulphide results in the production of elemental sulphur, water and nitric oxide - NO. When the catalyst is purged of sulphur by heating, the nitric oxide evolves. This
30 nitric oxide can then be trapped downstream, after air-oxidation to nitrogen peroxide and then used for other chemical reactions, such as the preparation of nitrates.

The advantage of this cycle is that the bed can be employed to first absorb the nitrogen peroxide, separating
35 it from a flue gas stream for subsequent recovery.

Combined Absorption of Oxides of Sulphur and Nitrogen

It has also been found that the catalyst can be activated by mixtures of NO₂ and SO₂ in an air stream, at ambient temperatures. When this catalyst is treated with
40 a stream of H₂S and subsequently heated, sulphur, water

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and nitric oxide all distill off.

Tests based on the activation of a $2(\text{Na}_2\text{S})/\text{ZnS}$ form of catalyst deposited in S-100 Alcoa spheres (at 1% loading, by weight) show a capacity for such a bed to
5 absorb up to 6% by weight of sulphur dioxide, 9.1% by weight of nitrogen peroxide and 6% of carbon dioxide, simultaneously. The gas stream used for this test contained 10-12% of CO_2 ; 4-6% of O_2 ; 1000-2000 ppm of SO_2 and 100-400 ppm of NO_2 . These ratios are typical for a
10 flue gas. The absorption capacities for each of these components do not appear to be substantially cross-related.

Absorption of Carbon Dioxide

Another environmentally-undesirable component of
15 stack gases is carbon dioxide, because of the so-called Greenhouse Effect. Tests show that catalysts prepared according to the invention absorb carbon dioxide strongly, without in any way affecting their ability to take up the oxides of nitrogen and sulphur.

20 Specifically, the absorption of carbon dioxide has been demonstrated by tests effected with the catalyst in its sodium sulphide/zinc sulphide form, with the sodium sulphide to zinc sulphide ratio being 2 moles of sodium sulphide to 1 mole of zinc sulphide. The catalyst was
25 coated one percent on alumina. From a stream containing CO_2 , SO_2 , and NO_2 , we have found that one metric tonne of the catalyst takes up 60 kg of CO_2 , 60 kg of SO_2 , and 91 kg of NO_2 .

The catalyst will retain 60 kg of CO_2 from the
30 stream at saturation, and continues to absorb SO_2 until 60 kg of this compound has been removed from the stream. The absorption of NO_2 then continues until 91 kg of this oxide had been recovered. To prevent any SO_2 from escaping under these conditions, an additional
35 catalyst bed would be placed downstream to strip out any SO_2 leaving the first catalyst chamber by desorption.

When this exposed catalyst is treated with hydrogen sulphide, the oxides of sulphur and nitrogen react with the absorbed hydrogen sulphide, and convert the
40 sulphur oxides to sulphur and water. After reaction is

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complete, the catalyst contains elemental sulphur, nitric oxide, carbon dioxide and water. Heat treatment, at 400°C, drives off the sulphur, nitric oxide, and carbon dioxide. Each may be separately recovered downstream.

- 5 After the absorption stage is completed and the absorbed components have been treated with hydrogen sulphide, the spent catalyst is heated. Carbon dioxide CO₂ will be the first substance to desorb, and can be trapped by many standard methods. As the temperature
10 rises nitric oxide, NO will next come off, which substance can be converted in air to NO₂. This is an important industrial chemical when so isolated. It can be converted readily to nitrates, which are of importance for the fertilizer industry, for example. Finally, as the
15 catalyst temperature approaches 300°C, elemental sulphur will begin to distill off as another important industrial product. The bed may be re-exposed to a reducing gas. The catalyst will then be ready for another absorption cycle in the stack gas stream.

20 Desorption Runs - Effects of Physical Absorption of H₂

Returning to the absorption of hydrogen sulphides, from the results of the tests performed, it was determined that hydrogen sulphide was believed to be both physically and chemically absorbed within alumina-based catalysts.

- 25 Tests on a blank alumina support, containing no active ingredients, indicated that virtually all absorbed hydrogen sulphide could be driven out of such a support by heating it to 350°C under a sweep gas for a period of time of 90 minutes. Supports that had been impregnated with
30 ingredients to form the catalyst showed a tendency not to have released as much hydrogen sulphide at that temperature as did the blank support.

- Figure 1 shows this effect in which a blank Alcoa (S-100) alumina support is compared with catalysts
35 prepared by Method 1 with Zinc and Potassium sulphide; Zinc, Copper and Potassium sulphides, and Copper and Potassium sulphides all on the same type of S-100 support. All beds were loaded to saturation and then treated in the

- 19 -

sweetening phase for 90 minutes at various temperatures. Figure 1 shows the percentage of the hydrogen sulphide evolved, as a function of temperature after heating for 90 minutes at various temperatures.

- 5 Table 1 summarizes the data depicted in Figure 1 and adds the accumulated percent decomposition obtained both after the 90 minute heating at a constant temperature and after the final regeneration at 400°C. These percentages are based in both cases on conversion of
- 10 sulphur, being the mass of sulphur vaporized divided by the mass of sulphur available in the quantity of hydrogen sulphide originally absorbed.

Table 1

15 Effect of Heating at Various Temperature on
Hydrogen Sulphide Desorption and Decomposition
for Saturated Catalyst/Beds

	Catalyst /Bed	Heating Temp (°C)	% Desorption H ₂ S	% Sulphur Conversion	
			After Heating	After Heating	Total after Regeneration
20	Blank				
	Crushed				
	Alcoa				
	Support				
	#S-100	18°C	35	--	--
25		100	73	--	--
		150	82	--	--
		200	83	--	--
		250	93	--	--
		300	93	--	--
30		325	94	--	--
		350	100	--	--
	Zinc -				
	Sodium	18	42	--	1.6
35	Sulphides	100	70	--	7.8
		150	80	--	10.3
		200	83	--	17.2
		250	90	1.6	10.2
		300	87	3.3	10.2
40		350	88	7.0	7.5
		400	93	6.1	6.1

- 20 -

(Table 1 Continued)

	Zinc				
	Copper -	18	n/a	--	2.6
	Sodium		68	--	14.7
5	Sulphides	200	79	--	9.8
		300	81	3.2	10.8
		350	94	5.3	6.3
		400	96	3.2	3.2
<hr/>					
10	Copper-				
	Sodium	18	42.1	--	8.2
	Sulphides	350	95.7	1.1	1.5

(Heating Time: 90 minutes)

Partial Runs

15 The foregoing data on saturated catalyst beds give a clear indication that decomposition is occurring by the quantities of elemental sulphur that are produced. However, the decomposition effect is being masked by the hydrogen sulphide that is being physically absorbed, and then being desorbed without decomposing. The masking effect of physically absorbed hydrogen sulphide can be largely eliminated by exposing the catalyst to hydrogen sulphide streams for periods of time less than that necessary to saturate the bed. These are called "partial runs". In such partial runs, the amount of hydrogen sulphide evolved on regeneration was substantially reduced. Correspondingly, higher percentage figures for the amount of available sulphur in the hydrogen sulphide converted to elemental sulphur were obtained.

20 The catalyst, when used in association with microporous supports such as alumina or zeolite, rapidly absorbs hydrogen sulphide. It may be that the rapidity with which the hydrogen sulphide is absorbed permits the catalytic bed, at suitable flow rates, to saturate progressively when exposed to a sour gas stream. If the sweetening phase is terminated with only a portion of the bed exposed (and saturated) with hydrogen sulphide, then, as heat is applied to the bed in the presence of a sweep gas absorbed hydrogen sulphide that may be desorbed is swept into a region of the bed containing unexposed

- 2I -

catalyst. Consequently, a bed that is partially loaded to saturation along only a portion of its length would be capable, in the separation phase, it is believed, of exposing virtually all of the hydrogen sulphide to

5 chemical-absorption leading to decomposition.

Thus, on whatever basis, it has been found that with appropriately chosen partial loadings, it is possible to obtain virtually 100% dissociation of the hydrogen sulphide.

10 Tested Catalyst Variants

The dissociative capacity of different catalyst formulations were tested and some of the results obtained were as set out in Tables 2 and 3.

TABLE 2

	CATALYST (including method of preparation)	LOADING (gms/100 gms and as a % of saturation)	% SULPHUR CONVERTED (cumulative, at 400°C)
15	Zn-K-1C-1	0.6(20%)	>90%
	Zn-K-2W-1	0.7(23%)	>80%
20	Cu-K-1W-2	1.4(100%)	>70%
	Mn-K-1C-1	0.6(20%)	>90%

(Catalyst designation code:

	Zn	-	K	-	1C	-	1
	main		alkali		carrier:		method of
25	amphoteric		metal		1 - Alcoa		preparation
	or polyvalent				2 - ICI		1 - method 1
	metal				c - crushed		2 - method 2
					w - whole		using a
							sulphate)

30 The data in Table 2 provides quantitative figures on the extent of decomposition of hydrogen sulphide obtained, stated in terms of the percent conversion to sulphur.

Table 3 lists combinations of further ingredients all found to produce non-quantified but definite amounts
35 of elemental sulphur upon the consecutive exposure of the

- 22 -

catalytic bed to a 10% hydrogen sulphide/90% nitrogen gas stream at ambient temperature 18°C), followed by regeneration of the catalyst at temperatures ranging from 350-400°C as previously described. All runs were carried out using as a support the Alcoa alumina carrier No. S-100. All of the samples listed in Table 3 were prepared from sulphides in accordance with the procedure of Method 1.

The column entitled "Absorptive Capacity" indicates the percentage ratio of mass of sulphur absorbed to the mass of catalyst, at the point where the catalyst bed ceased to fully absorb further hydrogen sulphide (as tested by the darkening of lead acetate paper at the column exit).

15

TABLE 3

	Metal	Alkali Metal	Elemental Sulphur Detected	Absorptive Capacity (% sulphur loaded per mass of catalyst)
	Zinc	Sodium	Yes	2.4
20	Zinc	Potassium	Yes	1.4
	Iron	Sodium	Yes	2.4
	Vanadium	Sodium	Yes	2.3
	Copper (I)	Sodium	Yes	2.9
	Copper (II)	Sodium	Yes	2.0
25	Copper (II)	Sodium*	Yes	2.4
	Copper (II)	Potassium	Yes	2.2
	Nickel	Sodium	Yes	2.9
	Molybdenum	Sodium	Yes	2.3
	Aluminum	Sodium	Yes	2.7
30	Manganese	Sodium	Yes	2.8
	Manganese	Potassium	Yes	2.3
	Cobalt	Sodium	Yes	n/a

*2 moles of sodium

Tested Catalyst Variants - Mixed Catalysts

35

A number of combined catalysts incorporating two or three amphoteric and/or polyvalent metals have been tested. Table 4 sets out the absorptive capacity at room

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temperature for all such catalysts based on the alumina support, Alcoa No. S-100. In all cases the catalyst was prepared by Method 1 using a sulphide of the metal as the initial salt. All components were incorporated into the support in equal molar ratios.

TABLE 4

	Metal Components	Alkali Component	Absorptive Capacity (gms sulphur equivalent from H ₂ S in 100 gms catalyst)
10	<hr/>		
	Iron & Zinc	Sodium Sulphide	2.3
	Iron, Copper & Zinc	Sodium sulphide and Sodium hydroxide	2.2
15	Manganese & Zinc	Sodium sulphide and Sodium hydroxide	2.0
	Manganese & Zinc	Sodium sulphide	2.3
	Manganese & Nickel	Potassium sulphide	1.5
	Manganese & Molybdenum	Potassium sulphide	1.7
20	Iron & Zinc	Potassium sulphide	1.2

In all of the cases listed in Table 4, sulphur was observed to be evolved when the catalysts were regenerated at a temperature of 400°C.

Description of Examples Using Sulphur Dioxide

25 A two-to-one molar ratio of sodium sulphide to zinc sulphide was deposited on S-100 Alcoa Alumina Spheres. The amount of such components deposited was set, for two different samples, at 1% and 2% by weight of the final loaded support.

30 One hundred grams each of the two classes of catalyzed support, along with pure, crushed S-100 spheres were then progressively loaded with sulphur dioxide at room temperature by exposure to a stream of 18%

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concentration by volume of SO_2 in nitrogen; and then exposed to a stream of methane containing 10% by volume of hydrogen sulphide. The amounts of sulphur-equivalent absorbed and then converted to sulphur are shown in Table 5 where a comparison to a blank alumina support is also provided.

TABLE 5

SO_2 & H_2S Loading and Regeneration Data
For Al_2O_3 , 1% and 2% - $2(\text{Na}_2\text{S}):\text{ZnS}$
under Saturation conditions

10

Run No.	Bed	SO_2 Loading	H_2S Loading	Total S Loading	% Conversion
15	1. Al_2O_3 (crushed)	3.3	5.3	8.6	77
	2. Al_2O_3 (crushed)	3.1	5.3	8.4	72
	3. Al_2O_3 (crushed)	3.1	5.2	8.3	66
20	4. Al_2O_3 (crushed)	3.4	5.1	8.5	75
	5. 1% Catalyst	4.2	7.7	11.9	82
25	6. 1% Catalyst	4.7	6.9	11.6	82
	7. 1% Catalyst	4.6	7.3	11.9	79
	8. 1% Catalyst	4.6	7.3	11.9	79
	9. 1% Catalyst	4.6	7.4	12.0	79
30	10. 2% Catalyst	4.4	7.9	12.3	83
	11. 2% Catalyst	4.4	7.3	11.7	79
	12. 2% Catalyst	4.6	7.2	11.8	78
	13. 2% Catalyst	4.3	6.5	10.8	80

35 SO_2 and H_2S loading figures are in grams of Sulphur per 100 g of catalyst.

In order to determine if the absorptive capacity of the catalyzed supports changed over time, the 1% loaded and blank alumina samples of Table 5 were saturated by exposure to consecutive streams of 1.9% sulphur dioxide,

40

- 25 -

and 6.7% oxygen, both in methane, at room temperature, for one hour each. These samples were then allowed to stand at room temperature for 70 hours in sealed moisture-proof containers.

5 Table 6 shows the data obtained when these aged samples were exposed to hydrogen sulphide on the same basis as previously. From Table 6 it is apparent that the bare alumina absorbed a smaller quantity of sulphur dioxide than in the earlier tests, after exposure to this
10 aging test, but the catalyzed beds was unaffected.

TABLE 6

Loading and Regeneration Data for the SO₂ Saturated Beds
After Soaking for 70 hrs at Room Temperature

15	Run No.	Bed	SO ₂ Loading	H ₂ S Loading	Total S Loading	% Conversion
	1.	Al ₂ O ₃	2.7	4.2	6.9	68
	2.	1% catalyst	4.8	6.8	11.6	80
20						

During the sweetening runs with beds activated with SO₂ it was found that some sulphur dioxide was evolving and finding its way into the effluent gas. As much as 28% of the sulphur dioxide would become desorbed
25 at 150 psi. This is believed to be due to the highly exothermic character of the reaction of hydrogen sulphide and sulphur dioxide.

To reduce this effect, tests were run with the beds only partially saturated with SO₂ (i.e.: to 75% of
30 capacity). Utilizing beds of catalyst one percent by weight of 2(Na₂S):ZnS on S-100 Alcoa spheres that had been only partially saturated in this manner, a series of sweetening and conversion cycles were run at varying pressures. The results are set out in Table 7.

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TABLE 7
H₂S Loading As A Function of Pressure For The
Partially SO₂-Loaded Beds

Run No.	Pressure	SO ₂ Loading	H ₂ S Loading	Total S Loading	% Conversion
1.	150 psi	5.9	10.4	16.3	85
2.	150 psi	6.0	10.4	16.4	88
3.	80 psi	3.9	8.4	12.3	80
4.	80 psi	3.9	7.7	11.6	81
5.	40 psi	3.6	6.8	10.4	7
6.	40 psi	3.8	6.6	10.4	7

In the runs depicted in Table 7, no sulphur dioxide was evolved until just before break-through of the hydrogen sulphide occurred, and even then only trace amounts were detected.

Table 7 shows sulphur conversion ratios that are on the same order as those of Table 5. Further, the increased absorptive capacity of the catalyzed support under pressure is also shown.

The actual dependence of absorptive capacity under a range of pressures was also determined using a 1% loading of 2Na₂S/ZnS deposited on S-100 supports that were progressively saturated with sulphur dioxide and then saturated with hydrogen sulphide, both to the point of breakthrough. The results are shown in Table 8. These results are reproduced graphically in Figure 2.

TABLE 8

Loading As A Function of Pressure for
the Catalyst 2Na₂S/ZnS

Run No	Pressure	SO ₂ Loading	H ₂ S Loading	Total S Loading
		(as % S)	(as % S)	
1.	14.7 psig	4.6	7.3	11.9
2.	54.7 psig	5.0	8.1	13.1
3.	94.7 psig	5.9	9.2	15.1
4.	164.7 psig	10.3	9.6	19.9

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If we assume that the reaction occurring in the catalyst between hydrogen sulphide and sulphur dioxide is $\text{SO}_2 + 2\text{H}_2\text{S} \rightarrow 3\text{S} + 2\text{H}_2\text{O}$, then, expressed as weight of sulphur, sulphur dioxide will oxidize twice its weight of hydrogen sulphide. Thus we see in Table 8 that above a pressure of ca 100 psig, the loading of sulphur dioxide is exceeding that required to oxidize the hydrogen sulphide absorbed. Consequently, at higher pressures, it is preferable that the catalyzed support be only partially saturated with sulphur dioxide. This will avoid the evolution of excess sulphur dioxide while still providing a stoichiometrically sufficient amount of sulphur dioxide to react with the hydrogen sulphide that can be absorbed.

Throughout the foregoing tests, during the sulphur purging stage, tests for the presence of hydrogen sulphide in the sweep gas were made. In the process described which relied on the depositing of molecular oxygen within the catalyst, quantities of hydrogen sulphide were released at this stage. By the process described herein of activating the catalyst with sulphur dioxide, the release of hydrogen sulphide from the catalyst can be greatly reduced.

In the oxygen-activated process, it is believed that the activation stage did not produce activated sulphur sites at all possible locations within the micro-porous support, to the exclusion of sites capable of absorbing hydrogen sulphide. Consequently, during the process of exposing hydrogen sulphide to the catalyst to effect dissociation, considerable quantities of hydrogen sulphide became absorbed without becoming dissociated.

In the oxygen-activated process, the catalyst was cyclically exposed to the steps of being saturated with hydrogen sulphide, then regenerated by purging it of water and elemental sulphur (at 350°C), and then reactivated by exposure to air (at 200°C). Due to the fact that some hydrogen sulphide was merely absorbed within the catalyst, this substance became released in the purge cycle, contaminating the sulphur vapour being released and causing exfoliation of such sulphur. These effects were due to the presence and release of undecomposed hydrogen

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sulphide that was able to accumulate within the catalytic support in the oxygen-activated process.

In the sulphur dioxide-activated process, activation of the catalyst is effected by exposing the micro-porous support to sulphur dioxide. It is believed that this procedure is more efficient in forming active sites that are capable of dissociating hydrogen sulphide. This greatly reduces the amount of hydrogen sulphide that is absorbed and then released without being dissociated. When the catalyst has been activated by sulphur dioxide virtually no hydrogen sulphide appears in the regeneration phase.

The sulphur dioxide activation process relies upon the formation of a highly reactive sulphite within the micro-porous support. To form this sulphite, a metal must be present within the support. Water must also be present to allow the formation of the sulphite and the subsequent dissociation of hydrogen sulphide.

The sulphur dioxide activated process is capable of operating with a pure alumina support. The deposition within this support of an amphoteric or polyvalent metal sulphide, together with an alkali sulphide, enhances both the system's capacity to remove hydrogen sulphide from a gas stream, and its efficiency in converting hydrogen sulphide into sulphur.

With the deposition of a 1% loading by weight of zinc sulphide and sodium sulphide (in a 2:1 molar ratio) on a micro-porous alumina support, the absorptive capacity of the catalyst is enhanced 60% over that of pure alumina, and the efficiency of conversion to sulphur is increased by 50%. Tests have shown that the amount of sulphur absorbed (in the form of hydrogen sulphide) is increased from 8% by weight for pure alumina, to 12% by weight with the zinc and alkali sulphides present.

The quantitative runs to-date have utilized zinc sulphide. It is believed that even better performance, in terms of absorptive capacity and dissociation efficiency, will be obtained using manganese sulphide.

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Tests have been carried out with 1% loading ratios, by weight, for the metal and alkali sulphides on an alumina support. It is believed that superior performance will be obtained with a 2% loading.

5 Decomposition of Other Sulphur Compounds

While tests have been carried out mainly on hydrogen sulphide as the decomposed sulphide, it is believed that the catalyst will be active in decomposing organic-sulphur compounds such as carbonyl sulphide,
10 carbon disulphide, mono and dialkyl sulphides, alkyl-type disulphides and thiophene. It is also suitable for removing all of the foregoing from a mixture of more complex natural gas components in gaseous or liquid phase, such as from butane or propane, and including, generally,
15 natural gas liquids.

Supports

The principal support used in testing has been alumina in the form of Alcoa 1/4 or 3/4 inch spheres (#S-100). Other supports tested for absorptive capacity
20 include alumina in the form of Norton 5/16" rings (#6573), Norton spheres (#6576); CIL Prox-Svers non-uniform spheres, Davison Chemical molecular sieves (type 13x, 4-8 mesh beads), silica and char. The Alcoa support was chosen as the preferred carrier due to its high absorptive
25 capacity, which was due, in turn, to its large surface area (325m /gm).

The Alcoa support referenced is essentially alumina that is reported as being in the gamma and amorphous form. It is not believed that the type of
30 crystalline form in which the alumina may be found is of significance to the dissociative capacity of the catalyst.

Activity has been found where there is aluminum present in the support. The presence of aluminum in the support is relevant in that alumina will invariably be
35 formed. When preparing the catalyst, the alkali metal

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will attack the alumina and form alkali aluminate and species containing available reactive oxygen. Thus the aluminum-containing supports inherently are capable of providing active centres necessary to support the activity
5 of the catalyst. Such supports also provide an etchable base upon which actively catalytic sites are thought to be more likely to form.

Supports were tested for decomposition activity when aluminum was not present. A distinct but non-
10 quantified showing of production of elemental sulphur occurred on repeated cycles of exposure of an oxygen activated catalyst formed on a silica support, to a continuous stream of 10% hydrogen sulphide. This was based upon manganese and sodium as the active metal and
15 alkali respectively. Due to the reduced surface area of this latter carrier, only trace amounts of sulphur were produced, and no quantitative measurements of decomposition were made. However, this test demonstrated that it is not essential that the support upon which the
20 catalyst is based contain aluminum.

The capacity of the support to fully absorb hydrogen sulphide and/or other sulphur compounds is an important feature when it is desired to remove all significant traces of such compounds from a gas stream.
25 This characteristic is believed to be dominated by the support itself. When the production of sulphur is the primary objective, the efficiency of absorption by the carrier is less critical. In such cases supports may be used that do not effect 100% absorption of hydrogen
30 sulphide prior to saturation.

Improved performance is also anticipated where the metal and alkali sulphides are formed within the alumina of the alumina support, rather than just being deposited on the surface.

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Recyclability of the Catalyst

05 The prepared catalysts were run through at least 4 cycles of absorption and regeneration before quantified tests were carried out on them. These initial cycles were found appropriate to stabilize the catalyst and obtain relatively consistent results in subsequent tests. Generally, the activity of the catalyst in terms of its decomposing capacity increased following these preliminary recyclings.

10 No significant decline or loss of activity in dissociative capacity of the catalyst has been found despite a number of consecutive absorption and regeneration cycles so long as replacement oxygen is available. The absorptive capacity of the catalyst has
15 been shown to remain relatively unchanged through at least 30-40 cycles of absorption and regeneration.

Effects of Carbon Dioxide, Water and Heavy Hydrocarbons and Decomposition on Hydrogen Sulphide Absorption

20 When carbon dioxide is present in the gas stream it does not substantially affect the capacity of the catalytic bed to absorb hydrogen sulphide, but is itself absorbed. The presence of absorbed carbon dioxide within the bed does not significantly affect the decomposition of hydrogen sulphide.

25 When water is present in or exposed to the catalytic bed as a vapour component in a gas stream, the performance of the alumina-supported catalyst in terms of absorptive capacity is somewhat enhanced. Water has not been found, however, to have a significant effect on the
30 decomposing capacity of the catalyst.

When used to remove hydrogen sulphide from gas streams containing high boiling point hydrocarbons, contamination of the catalyst can occur. Prior scrubbing of the gas stream has been found necessary to reduce the
35 effects of this problem.

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Pressure, Flow Rate and Sweep Gas Effects on
Absorptive Capacity for Hydrogen Sulphide

5 The absorptive capacity of the catalyst (in terms
of the ratio of the mass of hydrogen sulphide removed in
the absorption stage to the mass of the catalyst) is
relatively insensitive to the concentration of hydrogen
sulphide in the gas stream for concentrations of hydrogen
sulphide up to 10%. It rises, however, approximately
linearly with total pressure, up to at least 500 psig.

10 At modest flow rates, the rate of removal of
hydrogen sulphide by absorption in the case of alumina
carriers is relatively high, up to the point where the
catalyst bed has been nearly totally saturated with
hydrogen sulphide at ambient temperature and pressure.

15 Some tests were done with a 3 minute residence
time. Other tests were done with a 0.7 minute residence
time. In both cases Alcoa alumina carriers impregnated
with the necessary ingredients to form the catalyst were
capable, before saturation, of removing virtually 100% of
20 the hydrogen sulphide from the gas stream. The level of
hydrogen sulphide prior to breakthrough was below the
threshold of measurability, in both cases being below 1
ppm.

Throughout most of the laboratory tests based on
25 re-oxygenation, nitrogen or methane containing small
amounts of oxygen was used as the carrier gas in most
cases to re-activate the catalyst after the sulphur had
been driven-off using oxygen-free nitrogen or methane as
the sweep gas. In some tests effected using a source of
30 sour natural gas as the sweep and carrier gas, the
hydrogen sulphide absorptive capacity of sample catalytic
beds (based on the Alcoa carrier) was similar to that
obtained with the nitrogen as the background gas. While
quantitative measurements of decomposing capacity were not
35 made in these latter tests, visual examination of the
catalyst bed after exposure to sour natural gas and before
regeneration showed clear deposits of yellow sulphur.
From this it is concluded that the substitution of natural
gas for nitrogen or pure methane as the background gas and
40 as the sweep gas does not significantly decrease the
absorptive or dissociative capacity of the catalyst.

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Conclusion

The foregoing has constituted a description of specific embodiments showing how the invention may be applied and put into use. These embodiments are only
5 exemplary. The invention in its broadest, and more specific aspects, is further described and defined in the claims which now follow.

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The embodiments of the invention in which an exclusive property or privilege is claimed are defined as follows:

1. A regeneratable catalytic composition comprising a support having associated therewith a non-gaseous, non-fluid substance capable of retaining and providing reactive oxygen for reaction with oxidizable substances brought into contact with such composition, and thereafter capable of being replenished with reactive oxygen by exposure to a source of oxygen.
2. A composition as in claim 1 wherein such composition contains reactive oxygen which has previously been provided to such composition by exposure to a conditioning fluid stream containing oxygen, excluding hydrogen peroxide.
3. A composition as in claim 1 wherein said composition has been depleted of reactive oxygen but can be reconditioned to contain reactive oxygen by exposure to a conditioning fluid stream containing oxygen, excluding hydrogen peroxide.
4. A composition as in claim 2 or 3 wherein the source of oxygen within the conditioning fluid stream is selected from the group of substances constituted by air, nascent oxygen, the oxides of sulphur and the oxides of nitrogen excluding nitrous oxide.
5. A composition as in claim 1 which has been depleted of reactive oxygen by exposure to a reducing gas.
6. A composition as in claim 5 wherein the reducing gas is hydrogen sulphide.
7. A catalytic composition as in claim 1 wherein said catalytic composition contains a mixture of at least two salts,
 - (a) one of said salts comprising at least one sulphide or selenide of at least one metal selected from the group of amphoteric or polyvalent metals, or mixtures thereof, and

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(b) the other of said salts being at least one sulphide or selenide of an alkali metal,

8. A catalytic composition as in claim 7 wherein the source of oxygen is selected from the group of substances constituted by air, nascent oxygen, the oxides of sulphur and the oxides of nitrogen excluding nitrous oxide.

9. A catalytic composition as in claim 7 or 8 containing reactive oxygen.

10. A catalytic composition as in claim 1, 3, 4, 5, 6 or 7 wherein the support is microporous, said support being capable of absorbing an oxide of sulphur.

11. A catalytic composition as in claim 1, 3, 5, 6 or 7 wherein the support is microporous, said support being capable of absorbing an oxide of nitrogen.

12. A catalytic composition as in claim 1, 2, 4 or 7 wherein the support is microporous, said support being capable of absorbing a non-oxide compound containing sulphur.

13. A catalytic composition as in claim 1, 2, 3, 5, 6, 7 or 8 wherein the support is alumina.

14. A method of decomposing a sulphur-containing compound from a fluid stream comprising:

(1) providing a fluid stream containing at least one sulphur compound having a non-sulphur component;

(2) exposing said stream at a temperature below the vapourization point of sulphur to a catalytic support within which has been deposited reactive oxygen derived from oxygen provided from the group of substances constituted by air, nascent oxygen, oxides of sulphur and the oxides of nitrogen, excluding nitrous oxide;

(3) heating said catalytic support at a temperature above the vapourization point of sulphur in the presence of a sweep gas to produce elemental sulphur.

15. A method as in claim 14 wherein the sulphur-containing compound is an organic compound.

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16. A method as in claim 14 wherein the sulphur-containing compound is selected from the group constituted by hydrogen sulphide, carbonyl sulphide, carbon disulphide, mono and dialkyl sulphides, alkyl-type disulphides and thiophenes.

17. A method of removing an oxide of sulphur from a fluid stream comprising:

- (1) providing a fluid stream, containing an oxide of sulphur;
- (2) providing a catalytic support which is capable of providing internally available reactive oxygen and which has been conditioned to absorb oxides of sulphur by prior exposure to a reducing gas to thereby deplete said support of internally available reactive oxygen;
- (3) exposing said stream to said catalytic support so prepared to permit the absorption of the said oxide;
- (4) converting a portion of said oxide of sulphur within said support to sulphur by exposing it to a reducing gas, and
- (5) purging said support of sulphur by exposing it to a sweep gas at a temperature above the vapourization point of sulphur.

18. A method of removing a higher oxide of nitrogen, being an oxide of nitrogen, excluding nitrous oxide, from a fluid stream comprising:

- (1) providing a fluid stream, containing a higher oxide of nitrogen;
- (2) providing a catalytic support which is capable of providing internally available reactive oxygen and which has been conditioned to absorb such higher oxide of nitrogen by being depleted of internally available reactive oxygen by the conditioning step of exposure to a reducing gas;
- (3) exposing said higher oxide to said catalytic support so prepared so as to permit the absorption of the higher oxide of nitrogen;
- (4) converting a portion of said higher oxide of nitrogen within said support to nitric oxide by exposing it to a reducing gas, and
- (5) purging said support of nitric oxide by heating the catalytic support.

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19. The method of claim 18 wherein the purging of the support of nitric oxide is carried-out in the presence of a sweep gas.

20. A method of removing carbon dioxide from a fluid stream comprising:

- (1) providing a fluid stream, containing carbon dioxide;
- (2) providing a microporous catalytic support which is capable of providing internally available reactive oxygen and which has been conditioned to absorb such carbon dioxide by being depleted of internally available reactive oxygen by the conditioning step of exposure to a reducing gas;
- (3) exposing said fluid stream to said microporous catalytic support so prepared so as to permit the absorption of carbon dioxide; and
- (4) purging said support of carbon dioxide by heating it to an elevated temperature.

21. A method as in claim 14, 15, 16, 17, 18, 19 or 20 wherein said catalytic support contains a mixture of at least two salts,

- (a) one of said salts comprising at least one sulphide or selenide of at least one metal selected from the group of amphoteric or polyvalent metals, or mixtures thereof, and
- (b) the other of said salts being at least one sulphide or selenide of an alkali metal.

22. A method as in claim 14, 15, 16, 17, 18, 19 or 20 wherein said catalytic support is microporous alumina and contains a mixture of at least two salts,

- (a) one of said salts comprising at least one sulphide or selenide of at least one metal selected from the group of amphoteric or polyvalent metals, or mixtures thereof, and
- (b) the other of said salts being at least one sulphide or selenide of an alkali metal.

1/2

EFFECTS OF TEMPERATURE ON
HYDROGEN SULPHIDE DESORPTION

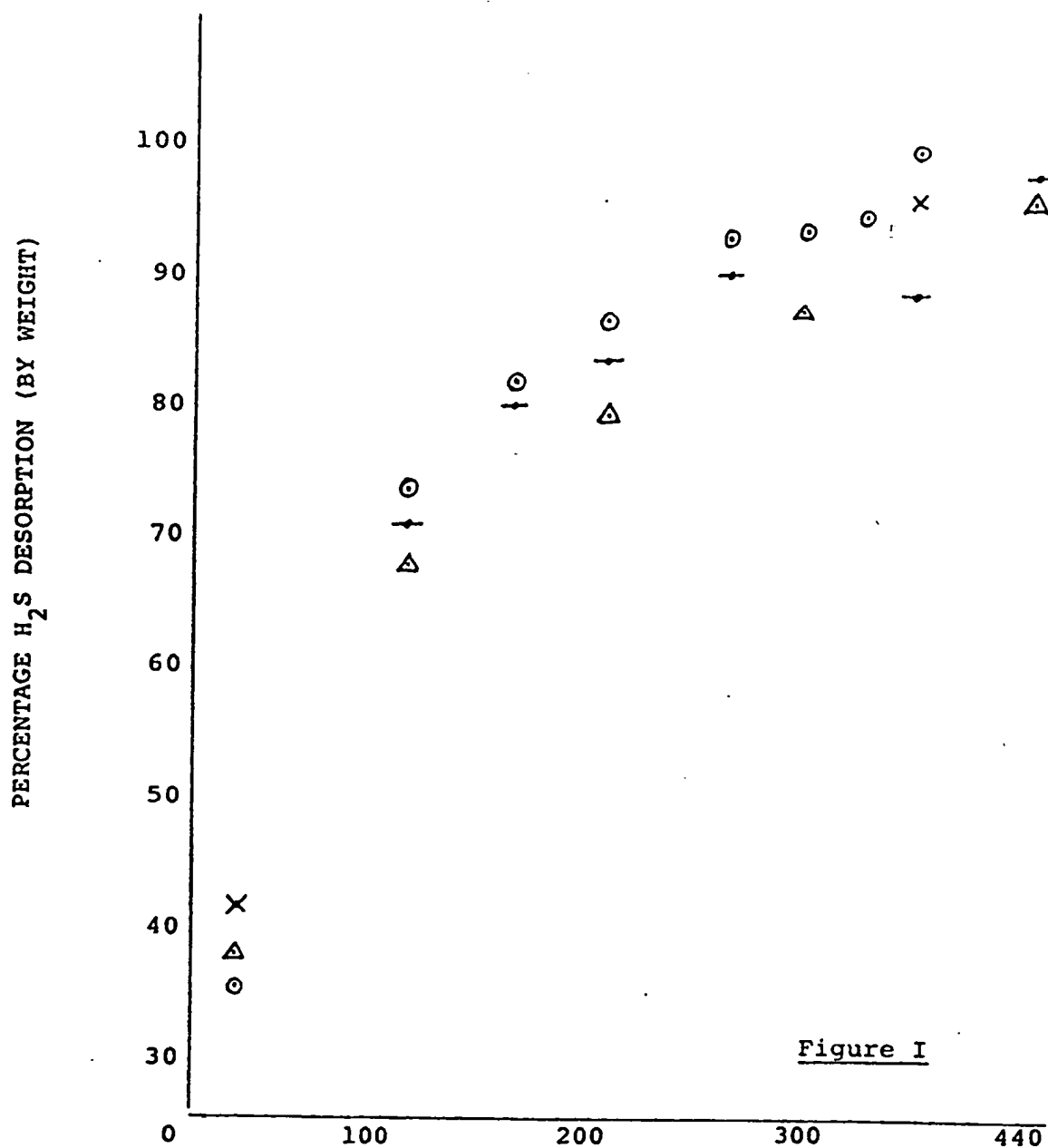


Figure I

KEY:

○ CRUSHED ALCOA CARRIER

+ ZINC CATALYST ON ALCOA CARRIER

△ ZINC-COPPER CATALYST ON
ALCOA CARRIER

X COPPER CATALYST

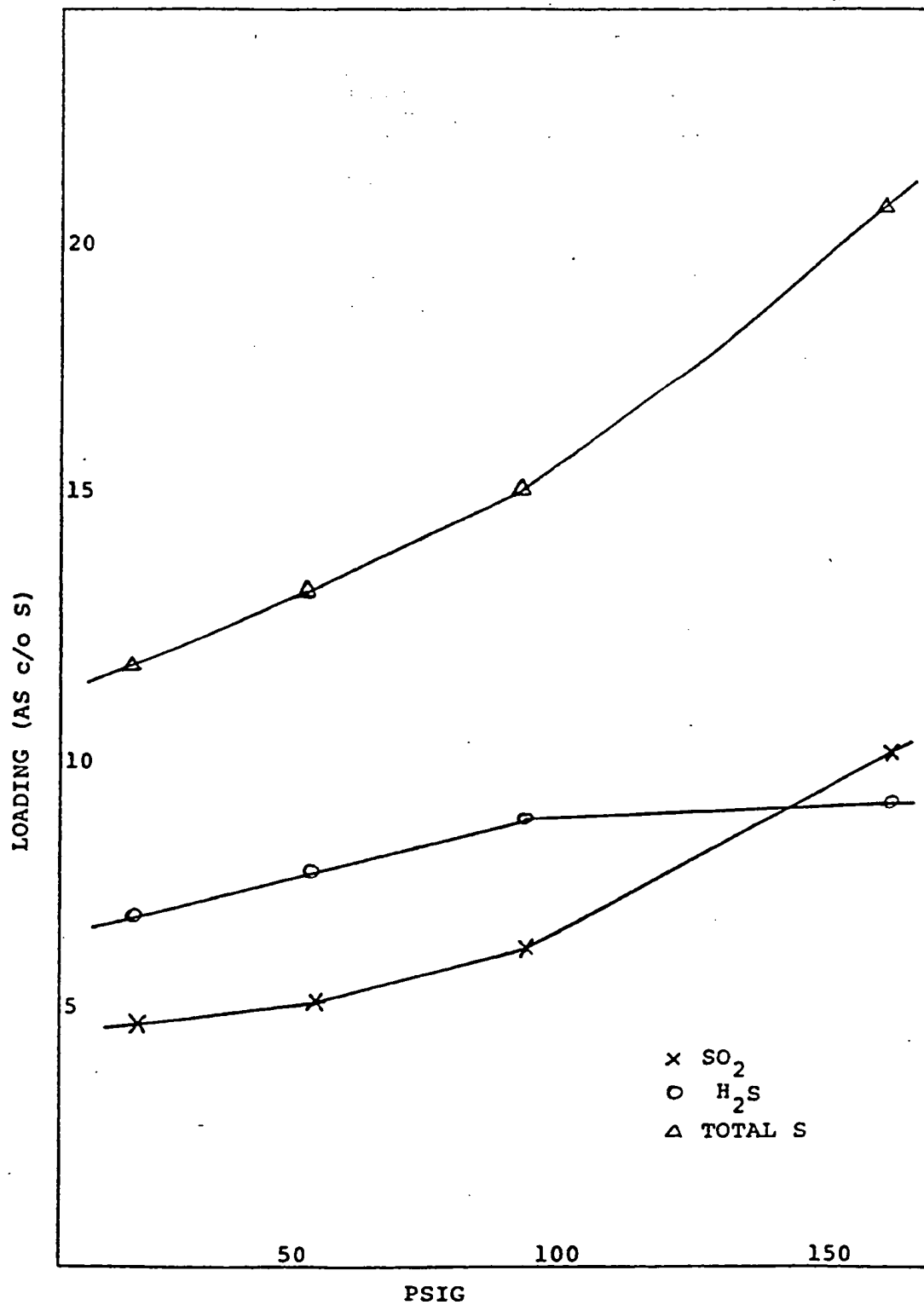
TEMPERATURE °C

SWEEP GAS: NITROGEN

FLOW RATE: 40 mls./mt.

DESORPTION

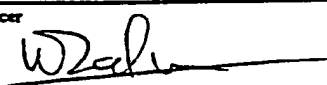
TIME: 90 MTS.

Figure 2

INTERNATIONAL SEARCH REPORT

PCT/CA 91/00160

International Application No

I. CLASSIFICATION OF SUBJECT MATTER (If several classification symbols apply, indicate all) ⁶		
According to International Patent Classification (IPC) or to both National Classification and IPC		
Int.Cl. 5 C01B17/04; B01J20/02	B01J27/04;	B01J27/057; B01D53/36
II. FIELDS SEARCHED		
Minimum Documentation Searched ⁷		
Classification System	Classification Symbols	
Int.Cl. 5	C01B ; B01J ; B01D	
Documentation Searched other than Minimum Documentation to the Extent that such Documents are Included in the Fields Searched ⁸		
III. DOCUMENTS CONSIDERED TO BE RELEVANT⁹		
Category ¹⁰	Citation of Document, ¹¹ with indication, where appropriate, of the relevant passages ¹²	Relevant to Claim No. ¹³
A	US,A,3 321 274 (SLAUGH) 23 May 1967 ---	
A	EP,A,0 324 091 (VEG-GASINSTITUUT) 19 July 1989 ---	
A	EP,A,0 071 983 (VEG-GASINSTITUUT) 16 February 1983 ---	
A	US,A,4 438 218 (BOORMAN) 20 March 1984 ---	
A	US,A,4 039 613 (KOTERA) 2 August 1977 ---	
A	GB,A,1 400 365 (MICHEL) 16 July 1975 ---	
<p>¹⁰ Special categories of cited documents :</p> <p>"A" document defining the general state of the art which is not considered to be of particular relevance</p> <p>"E" earlier document but published on or after the international filing date</p> <p>"L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)</p> <p>"O" document referring to an oral disclosure, use, exhibition or other means</p> <p>"P" document published prior to the international filing date but later than the priority date claimed</p> <p>"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention</p> <p>"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step</p> <p>"Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art.</p> <p>"&" document member of the same patent family</p>		
IV. CERTIFICATION		
Date of the Actual Completion of the International Search	Date of Mailing of this International Search Report	
30 JANUARY 1992	20.02.92	
International Searching Authority	Signature of Authorized Officer	
EUR PEAN PATENT OFFICE	ZALM W.E. 	

ANNEX TO THE INTERNATIONAL SEARCH REPORT
ON INTERNATIONAL PATENT APPLICATION NO. CA 9100160
SA 47162

This annex lists the patent family members relating to the patent documents cited in the above-mentioned international search report.
The members are as contained in the European Patent Office EDP file on
The European Patent Office is in no way liable for these particulars which are merely given for the purpose of information. 30/01/92

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EP-A-0071983	16-02-83	DE-A- 3131257 AU-B- 559024 AU-A- 8695982 CA-A- 1196477 JP-B- 3056772 JP-A- 58036620 US-A- 4478800	24-02-83 19-02-87 10-02-83 12-11-85 29-08-91 03-03-83 23-10-84
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US-A-4039613	02-08-77	JP-C- 834693 JP-A- 50071593 JP-B- 51011032 US-A- 3962409	18-11-76 13-06-75 08-04-76 08-06-76
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